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PESTICIDE SORPTION ON GEOLOGIC MATERIAL OF VARYING ORGANIC CARBON CONTENT

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Sorption of three pesticides on geologic material ranging in organic carbon content from 0.33 to 6.9 g kg⁻¹ was measured in soil columns using a miscible displacement technique. An octanol-water partitioning model was shown to be inappropriate for predicting sorption of the less hydrophobic pesticides on the low organic carbon materials.

INTRODUCTION

With increasing awareness of the importance of protecting ground water from contamination, there has been considerable interest in understanding the fate and transport of organic compounds in subsurface environments. Due to their detection in ground water, low polarity fuel components such as substituted benzenes and naphthalenes and chlorinated aliphatic solvents have been the focus of transport and transformation studies in the subsurface (Schwarzenbach, 1981; Banerjee, 1985; MacIntyre, 1985; Stauffer, 1986). In addition, widespread and continuous pesticide use coupled with the high water solubility and persistence of some pesticides has resulted in pesticide transport to ground water (Richard, 1975; Sandhu, 1978; Junk, 1980). As a result, organic contaminant transport in the subsurface is coming under increased scrutiny in the U.S.

There exists an extensive literature on organic compound sorption on geologic material. Many of these sorption data are for surface soils, or sediments, both of which have high organic carbon contents relative to subsurface geologic material from the unsaturated and saturated zone. Solute retention on natural organic carbon can be the result of both partitioning and adsorption, hence use of the general term sorption. For higher organic carbon sorbents and hydrophobic solutes, partitioning-like pro-

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2. Key words: hydrophobic partitioning, pesticides, sorption.

3. Abbreviations: BTC, breakthrough curves; CEC, cation exchange capacity; HPLC, high performance liquid chromatography; TOC, total organic carbon.

cesses predominate. As a result, good correlations have been observed between sorption on natural organic carbon and partitioning of organic solutes between water and organic solvents (Briggs, 1973; Karickhoff, 1979; Brown, 1981).

Recently, more sorption and transport studies with low organic carbon subsurface materials have appeared in the literature, and results of some of these studies have indicated that correlations developed between high organic carbon sorbents and sorption cannot always be extended to low organic carbon sorbents (Hassett, 1981; Schwarzenbach, 1981; Means, 1982; Banerjee, 1985). As a result, the concept of solute partitioning between an aqueous and hydrophobic phase (organic carbon) and predictive sorption equations based on solute aqueous solubility, hydrophobic surface area, octanol-water partition coefficients (K_{ow}), or other measures of solute hydrophobicity, need to be reevaluated (Mingelgrin, 1983).

The objectives of the research presented here were to evaluate the applicability of an organic partitioning model for predicting sorption at low organic carbon levels by measuring the sorption and transport of three pesticides on geologic material of varying organic carbon content.

METHODS

Methods. The sorbents used in this study were the $< 250\mu$ fractions of a surface soil from Florida, Eustis sand (Typic Quartzipsamments), and two subsurface geologic materials collected in south central Oklahoma. Subsurface material J10 was collected from the unsaturated zone at the 290 to 340 cm depth, and subsurface material N6 was collected from the saturated zone at the 417 to 478 cm depth. J10 and N6 were collected with a rotary drill rig at two sites 20 kilometers apart, both of which were overlaid with a Verdigris slit loam (Cumulic Hapludolls). Standard techniques (Klute, 1982, 1986) were used for determination of sorbent pH (1:1 0.01 M CaCl_2); total organic carbon, TOC (dry combustion); particle density (pycnometer); particle size distribution (hydrometer); and cation exchange capacity, CEC (Na saturation). (See Table 1 for relevant sorbent characteristics.) The three solutes used were analytical grade herbicides: hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione], atrazine [2-chloro-4(ethylamino)-6-(isopropylamino)-s-triazine], and diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]. The aqueous solubilities at 25°C for these compounds were 1.31×10^{-1} M, 3.25×10^{-4} M, and 1.80×10^{-4} M, respectively.

Miscible Displacement Experiments. The air-dry sorbents were hand-packed in glass, prep-scale liquid chromatography columns 25 mm i.d. and 50 mm long (column length is adjustable to 250 mm). The soil columns were wetted initially from the bottom very slowly (pore water velocity = 1.0 cm h^{-1}), with 0.01 M CaCl_2 to facilitate air displacement and minimize soil particle migration. When soil column wetting was complete, the 0.01 M CaCl_2 pore water velocity was increased to 20 cm h^{-1} until a

TABLE 1
Chemical and Physical Properties of the Sorbents and Columns

Sorbent	Organic carbon (g kg ⁻¹) ± 95% C.L.	Clay (g kg ⁻¹)	CEC [mmol (+) kg ⁻¹] ± 95% C.L.	pH (1:1 .01 M CaCl ₂)	ρ (Mg m ⁻³)	θ (m ³ m ⁻³)
Eustis	6.9 ± 0.6	145	22 ± 4	4.9	1.64	.373
J10	2.6 ± 0.1	135	110 ± 4	5.7	1.42	.464
N6	0.33 ± 0.01	200	90 ± 2	6.9	1.52	.432

minimum of 30 pore volumes had passed through the columns. Accurate flow rate control was achieved by using Waters 6000A high-performance liquid chromatography (HPLC) pumps and Isco Model 314 syringe pumps. To minimize extraneous solvent front mixing when initiating a miscible displacement, separate pumps plumbed into an inert four-way slider valve were used to deliver 0.01 M CaCl₂ or solutes in 0.01 M CaCl₂.

Solute breakthrough curves (BTC's) were plotted with pore volumes (cumulative effluent volume [V]/total column pore volume [Vo]) versus relative concentration (effluent concentration [C]/input concentration [Co]). Retardation factors (Rt) were computed by dividing the areas behind the BTC's by the area behind the ³H₂O tracer BTC. Sorption coefficients, K (L kg⁻¹), were then computed from:

$$Rt = 1 + (\rho K) \theta^{-1}$$

where ρ is the sorbent bulk density in the columns (Mg m⁻³) and θ is the volumetric water content (m³ m⁻³). Carbon normalized sorption coefficients (Koc) were computed from experimental values:

$$Koc = K (\text{sorbent organic carbon content in g g}^{-1})^{-1}$$

and from literature octanol-water partition coefficients (Kow) (Rao, 1980; Bouchard, 1985), using Briggs' equation (Briggs, 1973):

$$\log Koc = 0.52 \log Kow + 0.64$$

Solute Quantitation. Concentrations of ³H₂O were determined using liquid scintillation counting. Concentrations of all non-radiolabelled solutes, hexazinone, atrazine, and diuron, were determined using HPLC. The HPLC stationary phase was a 4 μ Nova-Pak C-18 column; the mobile phase was 41% methanol, 7% acetonitrile, flowing at 1.7 ml min⁻¹. The UV spectra for hexazinone, atrazine, and diuron were obtained using a Waters 490 programmable, scanning UV detector, and subsequently the analytical wavelengths used for detection of the pesticides were 247, 222, and 251 nm respectively.

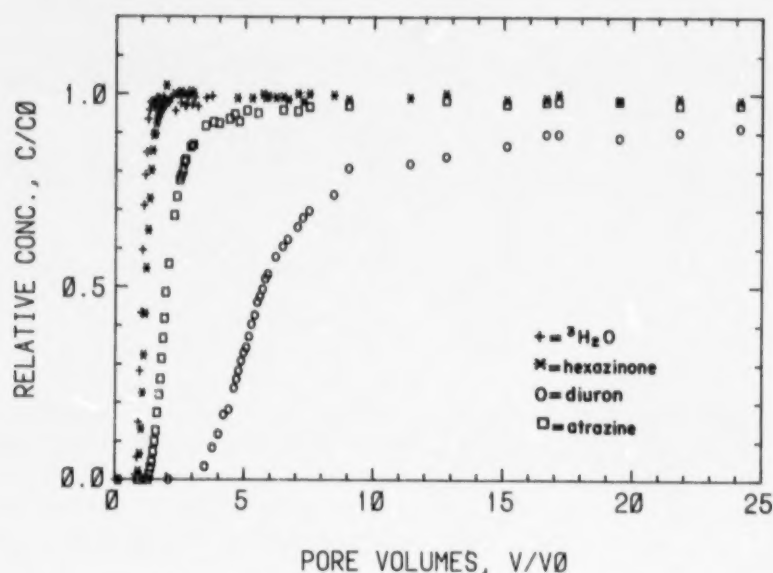


FIGURE 1. BTC's of $^3\text{H}_2\text{O}$ and the three pesticides on the highest organic carbon sorbent, Eustis surface soil.

RESULTS AND DISCUSSION

Asymmetric or tailing BTC's, where the effluent concentration (C) slowly approaches the input concentration (C_0), are indicative of nonequilibrium sorption during solute transport. Nonequilibrium sorption was observed for solute-sorbent combinations exhibiting the highest degree of sorption, i.e., diuron and atrazine on the Eustis soil, and diuron on the J10 subsurface material (Fig. 1, 2). These observations are consistent with those of other researchers who have noted that the rate of sorption $\propto K^{-1}$ (Karickhoff, 1985; Wu, 1986).

As a result of sorption's rate's dependence on K , when studying solute-sorbent combinations exhibiting a range of K values, all solutes will be at different points of approach to sorption equilibrium at a given sampling time. Miscible displacement techniques offer advantages over batch sorption techniques for obtaining accurate sorption equilibrium measurements because graphical extension of an asymmetric BTC (nonequilibrium conditions) to $C = C_0$, and determination of the area behind the BTC allows estimation of sorption under overall column equilibrium conditions. As a result, sorption equilibrium estimation using miscible displacement techniques

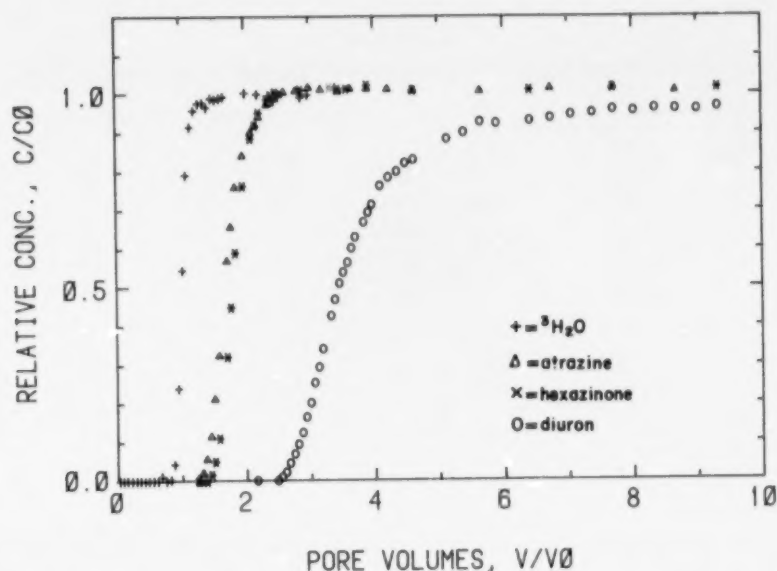


FIGURE 2. BTC's of $^3\text{H}_2\text{O}$ and the three pesticides on the intermediate organic carbon sorbent, J10 subsurface material.

avoids the long equilibration times needed in batch studies with highly-sorbed solutes and thus minimizes volatilization and degradation losses that can cause overestimation of sorption.

For the highest organic carbon sorbent used, Eustis surface soil, experimental K_{oc} values and K_{oc} values computed using Briggs' equation (Briggs, 1973) derived for high organic carbon sorbents were within a factor of two, indicating that the observed sorption was to Eustis organic carbon (Table 2). Briggs' equation is one of many empirical equations of the general form:

$$\log K_{oc} = a \log K_{sw} + b$$

where K_{sw} is the partition coefficient for organic solvent-water systems and a and b are empirical constants. These relationships are useful when, as described by solvophobic theory (Horvath, 1976), organic solute partitioning between the aqueous and organic phases is driven by a thermodynamically favorable entropy change in the aqueous phase, and when weak dispersion forces are the predominant organic solute-organic solvent interactions. When solute partitioning to natural organic is the dominant process for solute retention on geologic material, solute sorption will increase with solute hydrophobicity and sorbent organic carbon content. For the

TABLE 2
Sorption Coefficients (K) Computed from Miscible Displacement Data

Solute-Sorbent	K ^a	Koc Experimental	Koc Predicted
Hexazinone - N6	0.102	309	
J10	0.239	92	14
Eustis	0.066	10	
Atrazine - N6	0.040	121	
J10	0.216	83	73
Eustis	0.330	48	
Diuron - N6	0.074	224	
J10	0.964	371	127
Eustis	1.764	256	

^aSorption coefficient computed from $K = (Rt-1) \theta / \rho$.

Eustis soil, pesticide sorption increased with solute hydrophobicity as predicted by the partitioning model (Fig. 1, Table 2).

As on the Eustis soil, the most hydrophobic solute, diuron, was the most highly sorbed on the intermediate organic carbon J10 material. However, hexazinone and atrazine were similarly sorbed on the J10 material, which was a reversal of the sorption order on the higher organic carbon Eustis soil (Fig. 2, Table 2). Hexazinone is nearly three orders of magnitude more water-soluble than atrazine, so the hexazinone sorption could not be explained by solute partitioning to sorbent organic carbon.

Deviations from carbon-based sorption, as predicted by the partitioning model, increased for the lowest organic carbon sorbent, N6 aquifer material. On the N6 aquifer material, the most water-soluble, least hydrophobic compound, hexazinone, was the most highly sorbed (Fig. 3, Table 2). Experimentally determined Koc values for hexazinone varied by a factor of 30, increasing as sorbent organic carbon content decreased (Table 2). Clearly, solute partitioning to sorbent organic carbon was not the dominant process in hexazinone sorption on the N6 aquifer material. A similar, though less pronounced, inverse relationship between Koc and sorbent organic carbon content was observed for atrazine; however, no trend was apparent in diuron experimental Koc's which remained relatively constant (Table 2).

Therefore, it appeared that noncarbon-based sorption increased with solute hydrophilicity. This was an important observation because it indicated that the noncarbon-based sorption was probably due to site-specific interactions (a violation of a partitioning model assumption), rather than to nonspecific physical interactions with noncarbon mineral surfaces. If nonspecific physical interactions between the pesticides and mineral surfaces were major contributors to sorption, then similar increases in Koc with decreasing sorbent organic content would have been observed for all

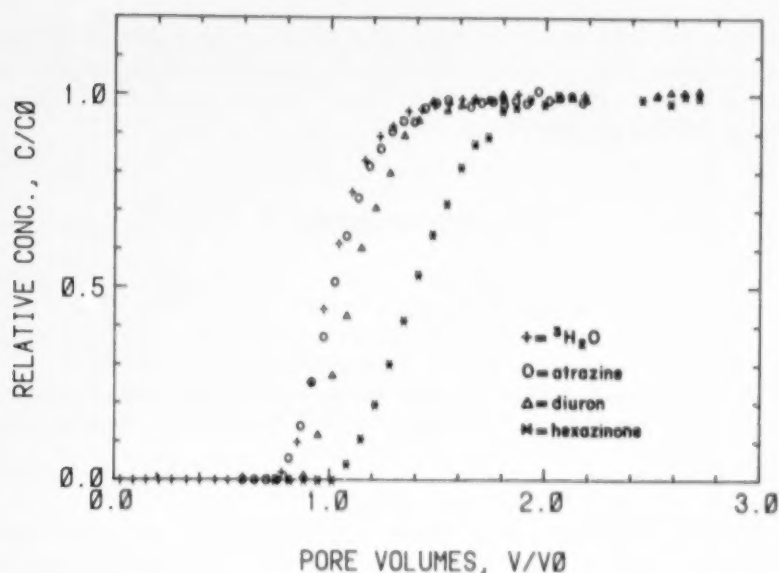


FIGURE 3. BTC's of $^3\text{H}_2\text{O}$ and the three pesticides on the lowest organic carbon sorbent, N6 aquifer material.

pesticides. A general term, perhaps based on mineral surface area and accounting for mineral surface interactions, could then be developed and incorporated into existing organic carbon partitioning models. However, the occurrence of solute and site-specific interactions obviates simple development of such a general term.

Most of the research on organic chemical interactions with mineral surfaces has been with commercially available clay minerals. These studies have often utilized vapor deposition techniques to study organic compound sorption on clay minerals in the absence of a solution phase. In the absence of liquid water, direct dipole-dipole and ion-dipole interactions are possible between polar organic solutes and clay mineral surfaces. However, in the presence of liquid water it is probable that the major interactions are hydrogen bonding and other dipole-dipole interactions between a polar organic solute and the coordination water of adsorbed inorganic cations (Mortland, 1986). For polar organic solutes, like hexazinone with two carbonyl moieties, dipole-dipole interactions may result in polar solute retention on hydrophilic mineral surfaces that exceeds that of more hydrophobic solutes.

In summary, this study has shown that the noncarbon-based, or mineral surface, sorption of polar solutes increased as solute hydrophilicity increased and as sorbent organic carbon content decreased. Though the magnitude of the mineral surface

interactions was not great when measured in 50-mm soil columns, deviations from noncarbon-based sorption could become significant over the long transport distances possible in aquifers and underscore the limitations of using partitioning models for predicting sorption of polar solutes on low organic carbon sorbents.

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